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Unprecedented multicomponent organocatalytic synthesis of propargylic esters via CO_2 activation

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Abstract: An efficient and straightforward organocatalytic method for the direct, multicomponent carboxylation of terminal alkynes with CO_2 and organochlorides, towards propargylic esters, is reported for the first time. 1,3-Di-tert-butyl-1H-imidazol-3-ium chloride, a simple, widely-available, stable, and cost-efficient *N*-heterocyclic carbene (NHC) precursor salt was used as the (pre)catalyst. A wide range of phenylacetylenes, bearing electron-withdrawing or electron-donating substituents, react with allyl-chlorides, benzyl chlorides, or 2-chloroacetates, providing the corresponding propargylic esters in low to excellent yields. DFT calculations on the mechanism of this transformation indicate that the reaction is initiated with the formation of an NHC-carboxylate, by addition of the carbene to a molecule of CO_2. Then, the nucleophilic addition of this species to the corresponding chlorides has been computed to be the rate limiting step of the process.

Introduction

Carbenes are neutral compounds bearing a divalent carbon atom having six valence electrons. Due to the fact that the number of carbene electrons deviates from the ‘‘octet rule’’, carbenes were initially considered to be non-isolable. The distribution of the carbenes’ electrons in their orbitals is the factor that defines their ground state, characteristics, and reactivity. More specifically, carbenes are of singlet or triplet ground state. In singlet carbenes, the two electrons that do not participate in *σ*-bonds occupy the highest occupied molecular orbital (HOMO) of the carbon atom. Therefore, the carbenic carbon’s p_π orbital is empty. This distribution of valence electrons makes singlet carbenes both nucleophilic and electrophilic at the same time. In contrast, triplet carbenes carry a single electron in each p_χ and p_ψ orbital and behave as biradicaloid species.[1]*N*-heterocyclic carbenes (NHCs) were successfully isolated and characterized for the first time by Arduengo in 1991.[2] The term NHC is used to describe molecules bearing the carbenic carbon in a ring containing at least one *α*-amino substituent.[3] The nitrogen atom at this position thermodynamically stabilizes the carbenic center of a singlet carbene, both due to its *π*-electron donating and *σ*-electron withdrawing character (Figure 1).[4]

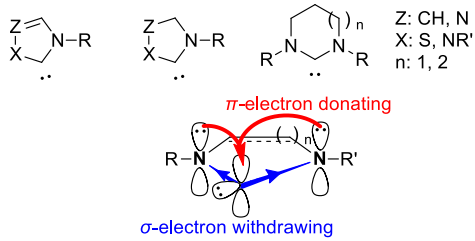
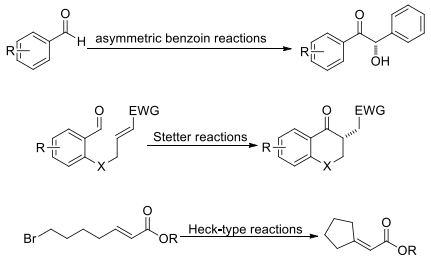


Figure 1. Some frequently encountered types of NHCs and the visualization of the stabilization of singlet carbenes originating from the *α*-amino substituent(s).

Among others, NHCs have been studied as ligands that can substitute phosphines in metal complexes. Indeed, many metal complexes of NHCs efficiently catalyze a plethora of reactions, including olefin metathesis and cross-couplings.[5]Moreover, catalytic systems of “green” metals, such as copper and iron, with NHCs as ligands find numerous applications in sustainable catalytic systems.[6] Equally important, NHCs serve as excellent organocatalysts in many organic transformations. The benzoin reaction is one of the earliest known carbon-carbon bond-forming reactions catalyzed by *N*-heterocyclic carbenes.[7]Ever since, NHCs organocatalysis has been employed in many different transformations. In addition to the benzoin reaction,[8] these include the Stetter reaction,[9] Heck-type reactions,[10] NHC-catalyzed umpolung of imines for intramolecular reactions, as well as many other valuable transformations employing NHCs’ peculiar behavior and balance between nucleophilicity and electrophilicity (Scheme 1).[11]



Scheme 1. Examples of useful organic transformations catalyzed by NHCs.

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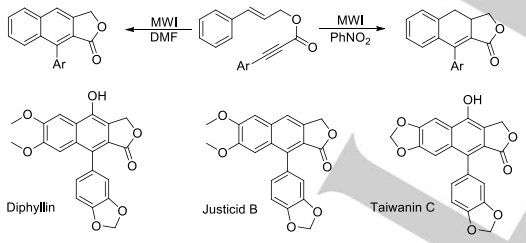
Recently-reported transformations, catalyzed by NHCs, deal with the utilization of nitroalkenes to prepare three- to five-carbon-atom building blocks,[12] the synthesis of 4-difluoromethylquinolines,[13] polymerization reactions,[14] 1,6-conjugate addition reactions,[15] Michael additions,[16] and various enantioselective functionalizations.[17]

On a different note, propargylic esters can be prepared via several synthetic pathways. One of the simplest methods involves the esterification of the corresponding propiolic acid. The desired propiolic acid has to be synthesized first, which is then coupled with the corresponding alcohol.[18] Propargylic esters can be also obtained from the transformation of lithium phenylacetylide, as demonstrated in the synthesis of Taxoids.[19] Other propargylic esters synthetic methods utilize carbon monoxide as the carbonyl source of the final molecule.[20] However, carbon monoxide is highly toxic and dangerous. Alternatively, carbon dioxide can be used as the source of the carbonyl group of the desired compounds. Besides leading to a highly useful family of organic synthons, these CO_2 monetization methodologies utilize one of the most harmful pollutants, the main “greenhouse effect” gas, transforming it into useful organic compounds.[21] Catalytic systems that are known to achieve the direct preparation of propargylic esters via CO_2 activation are currently based on rather complicated copper complexes or silver salts.[22,23] Note that propargylic esters are invaluable organic synthons, among others utilized in the preparation of arylnaphthalenes, via intramolecular dehydro Diels−Alder reactions (Scheme 2). Arylnaphthalenes and their dihydro- and tetrahydronaphthalene derivatives are compounds of medicinal interest, with a wide range of pharmacological activity. For example, diphyllin and justicidin B are both cytotoxic compounds and demonstrate anticancer, antiparasitic, and antiviral activities.[18d]

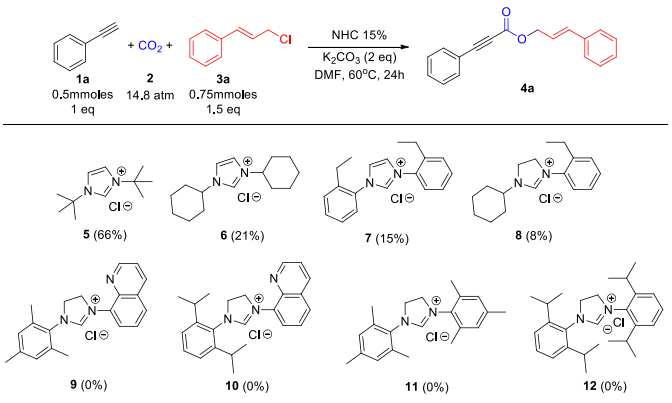


Scheme 2. Propargylic esters as valuable intermediates in organic synthesis. **18d**

Herein, we report a novel, straightforward organocatalytic approach for the multicomponent conjugation of terminal alkynes, carbon dioxide and organochlorides, affording propargylic esters with variable structural characteristics in a single step.1,3-Di-tert-butyl-1H-imidazol-3-ium chloride, a simple, widely-available, stable, and cost-efficient NHC precursor salt was used as the (pre)catalyst. The reaction between phenylacetylene, cinnamyl chloride and $CO_2$was the model reaction employed to probe the activity of a series of NHC salts as (pre)catalysts, as well as in order to determine the optimum reaction conditions. Then, a series of phenyl acetylene derivatives and organohalides were utilized to investigate the scope of the reaction. 18 different propargylic esters were synthesized and isolated, with isolated yields ranging from 25 to 97%. Finally, DFT studies were carried out to clarify the mechanism of the transformation. These studies suggest that the NHC moiety is crucial for the activation of CO_2 at the outset of the reaction, forming an NHC-carboxylate, which is then esterified with the allyl halide. In the last step, the NHC acts as an efficient leaving group, leading to the final adducts upon attack of the potassium acetylide. Thus, NHC is acting as a catalytic activator of CO_2, enhancing its nucleophilicity in the first step and its electrophilicity during the final alkyne attack.

Results and Discussion

To determine which NHC catalyzes the reaction most efficiently, a number of NHC salts precursors with variable structural characteristics were screened in the reaction between phenylacetylene (**1a**), CO_2 (**2**), and cinnamyl chloride (**3a**) towards propargylic ester **4a** (Scheme 3). K_2CO_3 was used as the base and DMF as the solvent, at 60°C and under 14.8 Atm of CO_2 pressure. NHC precursors utilized bear saturated (**8**-**12**) or unsaturated (**5**-**7**) NHC backbones, are of symmetrical (**5**-**7** and **11**, **12**) or unsymmetrical (**8**-**10**) nature with regards to their exocyclic substituents, have aliphatic (**5**, **6**), aromatic (**7** and **9**-**12**) or both aliphatic and aromatic exocyclic substituents (**8**), or even exocyclic substituents bearing heteroatoms able to act as base and/or nucleophile when appropriately rotated close to the carbenic center (**9**, **10**).NHC precursors bearing the aliphatic, bulky, electron-donating exocyclic substituents tert-butyl (**5**) and cyclohexyl (**6**) groups afforded the desired product in**66** and **21**% yields, respectively. The rest of the NHC precursors utilized, afforded very low yields of the targeted propargylic ester (**7**-**8**), or no product at all (**9**-**12**). Therefore, among the NHC salts tested in the model reaction, 1,3-di-tert-butyl-1H-imidazol-3-ium chloride (**5**) exhibits the optimum catalytic behavior. This was the NHC precursor we utilized in the rest of our studies.



Scheme 3. Investigation of the catalytic activity of *N*-heterocyclic carbene salt precursors. (Experimental conditions: NHC precursor 15 mol%, phenylacetylene 0.5 mmol, cinnamyl chloride 0.75 mmol, carbon dioxide 14.8 Atm, K_2CO_3 1 mmol, DMF 4 mL, temperature 60°C, reaction time 24h.Yields were measured by GC/MS.)

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With the most efficient NHC salt (pre)catalyst in hand, we investigated the influence of the other reaction parameters. More specifically, we investigated the influence of the base used, the solvent of the reaction, the catalytic amount of the NHC precursor, and the reaction temperature (Table 1). Among the bases used, in DMF, potassium carbonate provided the best results (Entry 3). Sodium carbonate provided the desired product, albeit with significantly lower yields (Entries 4 and 9). This result is attributed to the size and the nature of the counterion of carbonate. Sodium bicarbonate was found to be an inappropriate base for the reaction (Entry 1), as also did sodium hydroxide (Entry 5). Besides DMF, four other solvents were used to carry out the reaction. Those were toluene, acetonitrile, dichloromethane and tetrahydrofuran (Entries 6 to 11). When acetonitrile was used as the solvent (Entries 7 to 9) the targeted propargylic ester was formed efficiently, but in slightly lower yields than those observed in the case of DMF. All other solvents either did not yield the product at all, or the product was formed in traces. By increasing the NHC (pre)catalyst loading from 15 to 20% (Entry 12), phenylacetylene is quantitatively converted to the desired product, as was also observed under 25% catalyst loading (Entry 13). The reaction also takes place at room temperature (Entry 14) affording a 55% yield of the propargylic ester, which is, however, lower than the 99% GC/MS yield obtained at 60°C. In a series of blank tests, it was found that the presence of base (Entry 17), NHC precursor (Entry 18) and a high pressure of carbon dioxide (Entry 16) were all necessary for the three-component reaction to occur.

We then carried out a kinetic study, in order to find the optimum reaction time. More specifically, we studied the catalytic activity of our optimized organocatalytic system in the reaction of phenylacetylene (**1a**), CO_2, and cinnamyl chloride (**3a**) towards propargylic ester **4a** via GC/MS. The conversion to the product **4a** over time is represented in Figure 2. Interestingly, the reaction has a relatively long induction period of about 10 hours (about 20% conversion in the first 10 hours). This long induction period could be rationalized by the necessity for the formation of an important intermediate in the catalytic cycle, or by some kind of an off-cycle process (also see the discussion with regards to the theoretical calculations below). After the necessary induction period, the reaction speeds up, reaching completion in about 10 additional hours, that is, in 20 hours total reaction time.

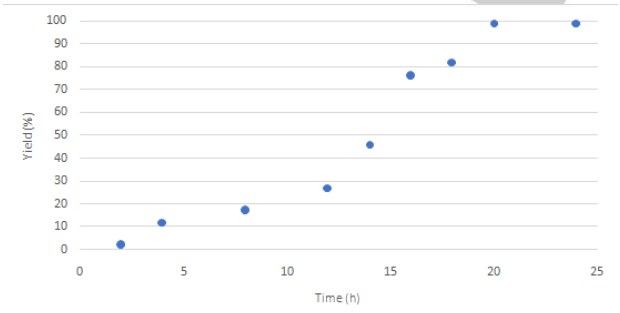
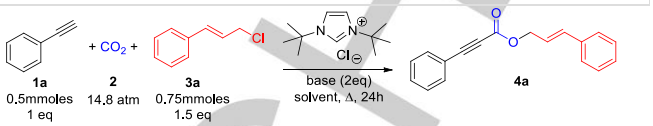


Figure 2. Reaction profile of the organocatalytic multicomponent coupling of phenylacetylene (**1a**), cinnamyl chloride (**3a**) and carbon dioxide towards propargylic ester **4a**.

Table 1. Investigation of the conditions of the three-component coupling of phenylacetylene, cinnamyl chloride and carbon dioxide towards the corresponding propargylic ester.



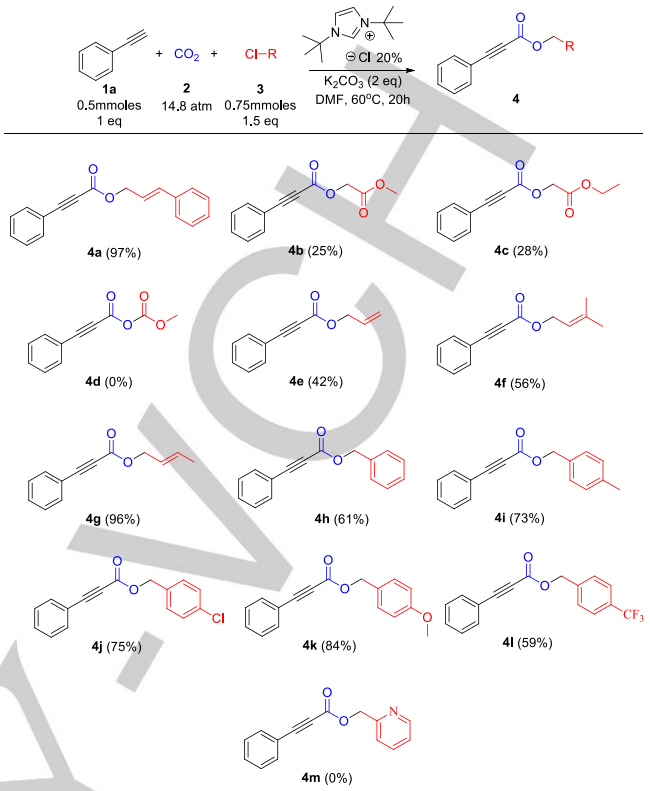
Entry	Base	Solvent	Catalyst loading	Temperature	Yield[a]
1	$NaHCO_3$	DMF	15%	60°C	-
2	CsF	DMF	15%	60°C	9%
3	K_2CO_3	DMF	15%	60°C	66%
4	Na_2CO_3	DMF	15%	60°C	11%
5	NaOH	DMF	15%	60°C	-
6	K_2CO_3	Toluene	15%	60°C	-
7	K_2CO_3	CH_3CN	15%	60°C	53%
8	K_2CO_3	CH_3CN	20%	60°C	78%
9	Na_2CO_3	CH_3CN	15%	60°C	Trace
10	K_2CO_3	CH_2Cl_2	15%	60°C	Trace
11	K_2CO_3	THF	15%	60°C	-
12	K_2CO_3	DMF	20%	60°C	>99%
13	K_2CO_3	DMF	25%	60°C	>99%
14	K_2CO_3	DMF	20%	r.t.	55%
15[b]	K_2CO_3	DMF	20%	60°C	-
16[c]	K_2CO_3	DMF	20%	60°C	17%
17	-	DMF	20%	60°C	-
18	K_2CO_3	DMF	-	60°C	-

[a] Experimental conditions:1,3-di-tert-butyl-1H-imidazol-3-ium chloride (NHC precursor salt), phenylacetylene 0.5 mmol, cinnamyl chloride 0.75 mmol, carbon dioxide 14.8 Atm, base 1 mmol, solvent 4 mL, reaction time 24h. Yields were measured by GC/MS.[b] In the absence of CO_2. [c] CO_2 pressure of 4.9Atm.

Prior to investigating the reaction scope, we also carried out a series of control experiments towards shedding some light on the possible role of the NHC in the generation of the acetylide. It is known that the deprotonation of phenylacetylene readily occurs in the presence of carbonates to provide the corresponding acetylide.[24] Nevertheless, carbenes have been also shown to be able to insert into C-H bonds.[25] Therefore, we were intrigued to study whether the in situ generated NHC could somehow increase the rate of the acetylide formation. Unfortunately, though, despite

our efforts to trap the generated acetylide under conditions analogous to our reaction conditions, our experiments were inconclusive in this regard.

With the optimum reaction conditions in hand, we investigated the scope of the organohalides (Scheme 4). The two 2-chloroacetate esters probed yield the corresponding coupling products **4b** and **4c**, albeit at relatively low yields. Moreover, organochlorides bearing the chlorine atom on the carbonyl carbon do not provide the desired propargyl ester, as found in the case of **4d**. On the contrary, allylic chlorides are very good substrates for this reaction, leading to propargylic esters **4a**, **4e**, **4f** and **4g** in good to excellent yields. The relatively low yield in the reaction of chloropropene (leading to propargylic ester **4e**) can be attributed to the fact that this substrate has a relatively low boiling point (46°C, while the reaction temperature is 60°C). The same rationale can be also true in the case of propargylic ester **4f** (56% yield), given that chlorobutene has a boiling point of 59°C, also lower that the reaction temperature. Along these lines, crotyl chloride, with a boiling point of 85°C, yields the corresponding propargylic ester **4g** in an excellent, 96% yield. Benzyl chlorides are also very good substrates under these conditions, leading to propargylic esters **4h** to **4l**, in isolated yields ranging from 59 to 84%. Picolyl chloride does not provide the targeted ester **4m**, most probably due to the existence of the pyridine moiety in its structure. This was shown during control experiments, in which the reaction of phenylacetylene with benzylchloride was completely quenched in the presence of one equivalent (in relation to benzylchloride) of pyridine - in the absence of pyridine this reaction provides propargylic ester **4h** in 61% isolated yield. Interestingly, in addition to the parent benzyl chloride (**4h**), both electron-poor (**4j** and **4l**) and electron-rich (**4i** and **4k**) benzyl chlorides afford very good yields, while the co-existence of a second chlorine atom on the aromatic ring (**4j**) does not impose any problem to the reaction. Note, finally, that all organobromides probed (results not shown: 1-bromobutane, bromoethene, 1-bromododecane, 3-bromopropanenitrile, 2-bromo-1-phenylethanone) were found to be unsuitable substrates for the reaction.



Scheme 4. Investigation of the scope of the reaction with regards to the organochloride. (Experimental conditions: 1,3-di-tert-butyl-1H-imidazol-3-ium chloride (NHC precursor salt) 20%, phenylacetylene 0.5 mmol, organochloride 0.75 mmol, carbon dioxide 14.8 Atm, K_2CO_3 1 mmol, DMF 4 mL, reaction time 20h, reaction temperature 60°C. All yields provided are isolated.)

Subsequently, the scope of the multicomponent organocatalytic coupling towards propargylic esters was investigated with regards to the terminal alkyne utilized. The results of this study are shown in Scheme 5. Alkyl-substituted terminal alkynes (results not shown: 1-pentyne and 3,3-dimethylbut-1-yne) do not afford the targeted propargylic esters under our protocol's conditions. The same is true for a hydroxyl-bearing alkyne we tested (results not shown: 2-methylbut-3-yn-2-ol), as well as a phenyl acetylene bearing a bromide (results not shown: 1-bromo-2-ethynylbenzene). Moreover, the electron poor, p-NO_2-substituted phenyl acetylene affords the targeted propargylic ester **4n**, albeit in traces. On the other hand, the p-CF_3-substituted phenyl acetylene, which is also electron-poor, gives an excellent isolated yield of 91% of propargylic ester **4s**. This finding suggests the reaction is not problematic with electron-poor terminal alkynes in general, but, most probably, it is not compatible with the -NO_2 moiety (also see the discussion that follows). Phenylacetylenes bearing no aromatic substituents or methyl and/or methoxy moieties on the aromatic ring are excellent substrates under our protocol, affording the corresponding propargylic esters in very good to excellent yields (**4a**, **4o**-**4r**, and **4t**-**4u**).

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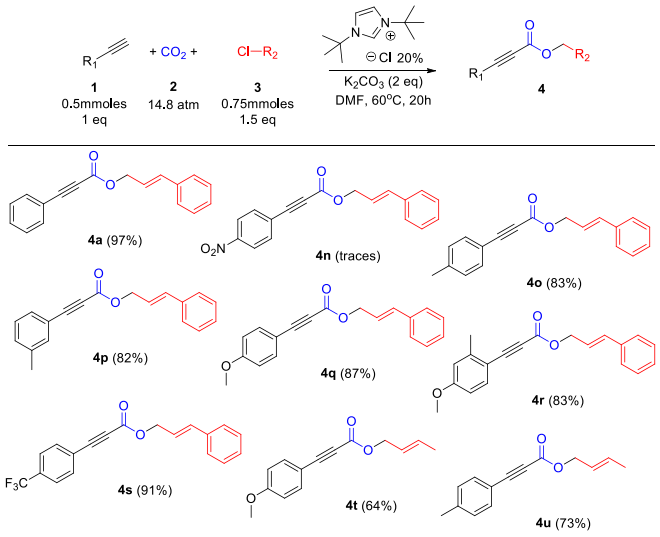

Scheme 5. Investigationof the scope of the multicomponent organocatalytic carboxylative coupling of terminal alkynes and organohalides with CO_2. (Experimental conditions: 1,3-di-tert-butyl-1H-imidazol-3-ium chloride (NHC precursor salt) 20%, terminal alkyne 0.5 mmol, organochloride 0.75 mmol, carbon dioxide 14.8 Atm, K_2CO_3 1 mmol, DMF 4 mL, reaction time 20h, reaction temperature 60oC. All yields provided are isolated.)

Theoretical Calculations

We next turned our attention to the study of the mechanism of the reaction, by means of DFT methods. The calculations were carried out with the Gaussian 16 set of programs, using the M06-2X functional together with the 6-311G(s,p) basis sets for full structure optimization. An implicit solvent model (IEFPCM, solvent = dimethyl formamide) was also incorporated to all calculations.[26]

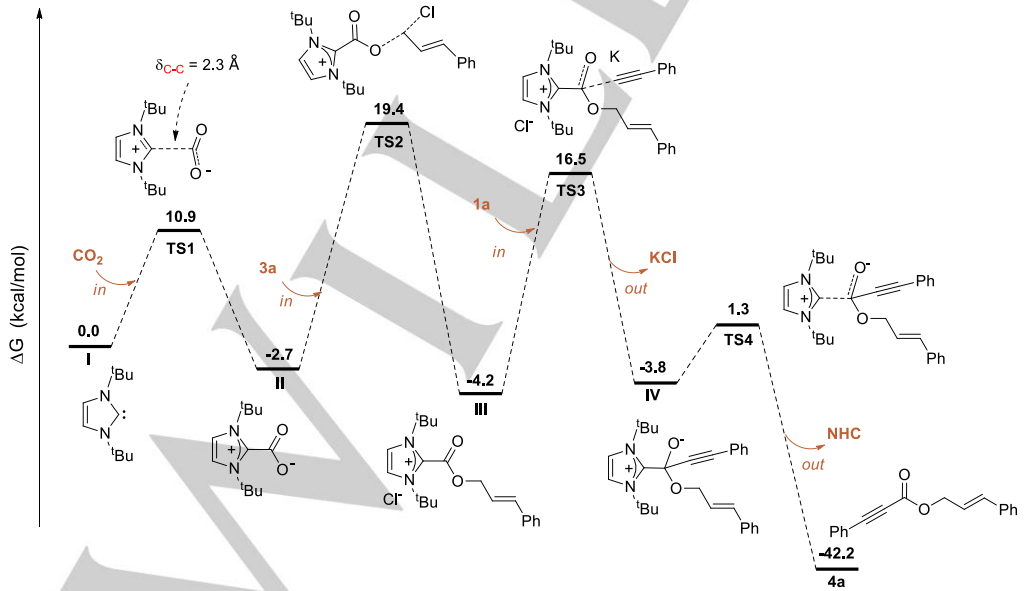

Figure 3. Energy profile for the catalytic cycle of the reaction between **1a**, **3a**, and CO_2.

We wanted to get information about the energy profile of the reaction, which is crucial to clarify some important issues about the mechanism, like: a) the identification of the rate limiting step of the process, b) the understanding of the origin of the induction period observed at the outset of the reaction, and c) the determination of the underlying reasons for the large difference of reactivity between the different electrophiles, like, for example, cinammyl chloride **3a***v*spicolyl chloride **3m** (Scheme 4). We assumed that the fundamental steps of the reaction would be the attack of the NHC catalyst to CO_2 (**TS1**, Figure 3), the S_N2-type nucleopilic substitution of the chloride by the carboxylate (**TS2**) and the final introduction of the propargylic system with concomitant recovery of the catalytic NHC carbene (**TS3** and **TS4**). For the initial calculations, those substrates affording the best results were selected, including the di-tertbutylcarbene catalyst derived from**5**, cinnamyl chloride **3a**, and phenylacetylene**1a**.

As previously mentioned, we envisioned that the first step of the reaction was the attack of NHC carbene to a molecule of CO_2 (Figure 3). As described by others,[27] this step was computed to be easy and low in energy (**TS1**, $\Delta G^{\ddagger}$ = 10.9 kcal/mol), with a very early transition state that bears a long carbon-carbon bond distance (2.3 Å). The intermediate formed in this step (**II**) is fairly stable and low in energy (-2.7 kcal/mol). These carbene-CO_2 adducts are known and extensively studied. Amongst others, they are used as non-ionic NHC precursors, delivering the free carbene in the reaction mixture upon thermal decomposition, circumventing the need for the use of a base.[28] The intermediate formed in step (**II**) shows kinetic resistance to react with cinnamyl chloride **3a**, as can be inferred from its moderate activation energy ($\Delta\Delta G^{\ddagger}$ = 22.1 kcal/mol). This value is perfectly affordable at the experimental reaction temperature. The structure of the transition state follows a standard S_N2-type nucleophilic displacement of the chloride anion (see 3D structure in Figure 4), leading to the second intermediate of the reaction (**III**), which is rather stable (ΔG = -4.2 kcal/mol). The process continues with the nucleophilic attack of the propargylic unit (**1a**) to intermediate **III** through a classical two-step addition to the carbonyl group (transition states **TS3** and **TS4**) with formation of the tetrahedral intermediate **IV**. The addition of the acetylide in **TS3** is higher in energy ($\Delta\Delta G$ = 20.7 kcal/mol) than the detachment of the carbene leaving group in **TS4**, which is very fast ($\Delta\Delta G$ = 5.1 kcal/mol), but both steps are lower in energy than **TS2**.

Thus, the energy profile points to the nucleophilic displacement of the chloride by NHC-carboxylate (**TS2**) as the rate limiting step of the process, as it shows the highest energy of the catalytic cycle. Thus, the comparison of the reactivity of the different substrates should be done at this point. In fact, we were able to locate the transition states for the substitution of intermediate II to benzyl chloride (**3h**) and picolyl chloride (**3m**). The computed structures of **TS2h**, and **TS2i** were structurally very similar to that of cinnamyl chloride **TS2a** (Figure 4).[29] The computed activation energies show the lowest value ($\Delta G^{\ddagger}$ = 22.1 kcal/mol) for the most reactive substrate of the three (**3a**), in agreement with the experimental results shown in Scheme 4. The activation energy for the benzyl derivative **3h** lies 0.9 kcal/mol higher, which is not a very significant difference, but enough to explain the decrease in yield noted experimentally (97% vs 61%, Scheme 4). Interestingly, the unreactive picolyl derivative **3m** shows an activation energy of $\Delta G^{\ddagger}$ = 24.7 kcal/mol). While this value is 2.6 kcal/mol higher than for **3a**, allowing us to explain a significant decrease in yield for substrate **3m**, it does not seem enough to account for its complete lack of reactivity. Therefore, the presence of a pyridine moiety has a deleterious effect on the reactivity by some other undisclosed mechanism. As previously discussed, the addition of 1 eq of pyridine to the reaction medium quenches the reaction completely. Finally, the structures of the three transition states in Figure 4 present forming O-C bond distances between 2.00 Å and 2.09 Å, and breaking C-Cl bond distances between 2.34 Å and 2.44 Å. Interestingly, the distances slightly increase with the increasing reactivity of the substrates (Figure 4). These data suggest that the reacting sp3 carbon develops a relative positive charge during **TS2**, explaining why electron donating substituents, like **3k**, show higher reactivity than electron withdrawing groups, like **3l** (Scheme 4).

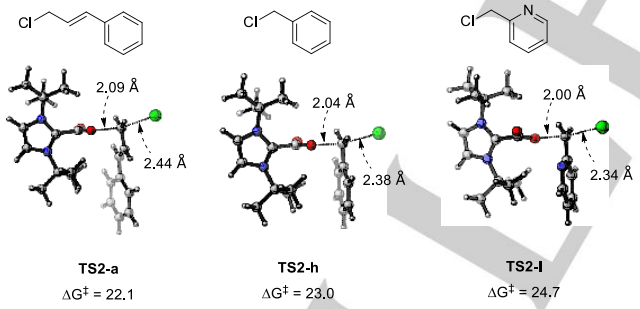

Figure 4. Activation free energies for the substitution step of chloride (**TS2**) in the cinnamyl (**3a**), benzyl (**3h**) and picolyl substrates (**3m**).

Finally, we were intrigued by the long induction period that we observed in our reactions (Figure 2). In fact, nothing, in the computed cycle shown in Figure 3, points to the existence of such an initial delay, which has to be related to some off-cycle process. One hypothesis is that the initial formation of the active NHC carbene from the imidazolium precursor in the presence of a base could be slow in the reaction scale, and, therefore, the necessary concentration of NHC carbene (I) would need some time to evolve.

Conclusions

A novel organocatalytic protocol for the multicomponent carboxylative coupling of terminal alkynes with organochlorides and CO_2, catalyzed by an in-situ generated NHC derived from the widely-available, cost-efficient and stable 1,3-di-tert-butyl-1H-imidazol-3-ium chloride was developed. The protocol is user-friendly, straightforward and highly efficient against a number of substrates and functionalities. In addition to the parent phenylacetylene, a wide range of substituted phenylacetylenes, bearing electron-withdrawing or electron-donating aromatic substituents, react with allyl-chlorides, benzyl chlorides, or 2-chloroacetates, providing the corresponding propargylic esters in low to excellent yields. DFT calculations on the mechanism of this transformation indicate that the reaction is initiated with the addition of the carbene to a molecule of CO_2, forming a NHC-carboxylate. This species is nucleophilic enough to react with chlorides, although the high activation energy of this process suggests that it is the rate limiting step. This fact would explain the large difference in reactivity of the different allyl and benzyl chlorides and the effect of the substituents.

Experimental Section

General reagent information. Unless otherwise noted, chemicals were obtained from commercial sources and were purified according to literature procedures. Solvents were purified according to published procedures, distilled and stored under argon over 3Å molecular sieves. All reactions were set up under argon and carried out under carbon dioxide in sealed, high pressure reactor. The course of the reactions was followed with GC/MS. The purification of the products was carried out by flash column chromatography, using silica gel 60 (230-400 mesh).

General analytical information. ^{1}H, ^{13}C NMR spectra were measured on a Varian Mercury 200MHz spectrometer using $CDCl_3$ as the solvent and its residual solvent peak as a reference. NMR spectroscopic data are given in the order: chemical shift, multiplicity (s, singlet, br. s, broad singlet, d, doublet, t, triplet, q, quartet, m, multiplet), coupling constant in Hertz (Hz), and number of protons. Peaks at 0 and 1.5ppm of spectra are attributed to impurities of laboratory solvents, organics, and gases in deuterated solvents.[30] HRMS spectra were recorded in a QTOF maxis Impact (Bruker) spectrometer with Electron Spray Ionization (ESI). The GC/MS spectra were recorded with a Shimandzu R GCMS-QP2010 Plus Chromatograph Mass Spectrometer using a MEGAR (MEGA-5, F.T: 0.25µm, I.D.: 0.25mm, L: 30m, Tmax: 350 ºC, Column ID# 11475) column, using *n*-octane as the internal standard.

Synthetic protocols. The synthetic protocols for NHC ligand precursors **5** to **10** are reported in the literature.[6b,31] NHC ligand precursors **11** and **12** were purchased and used without any further purification.

Unless otherwise mentioned, the following procedure was used for the synthesis of all products: A flame-dried vial with a stirring bar and a rubber septum was charged with 20 mol% of 1,3-di-tert-butyl-1H-imidazol-3-ium chloride (0.1 mmol), K_2CO_3 (1mmol) and DMF (4mL). Under a flow of argon, the terminal alkyne (0.5 mmol) and organohalide (0.75 mmol) were added and the mixture was placed in the pressure reactor. The reactor was purged three times with carbon dioxide, the pressure was finally fixed to 14.8 Atm and the reaction was allowed to stir in an oil bath, preheated at 60ºC, for 20 hours. After this time, the pressure reactor was cooled to

room temperature and ventilated carefully. Water was added to the reaction mixture and was extracted with ethyl acetate (3x5 ml). The organic phase was dried with $MgSO_4$ and the solvent was removed under reduced pressure to afford the crude mixture of the reaction. Gradient column chromatography with ethyl acetate/petroleum ether furnished the desired product. Products prepared for the first time were characterized by ^1H NMR, ^{13}C NMR, and HRMS, which are all in agreement with the assigned structures. Known compounds were characterized by ^1H NMR and ^{13}C NMR with all their spectroscopic characteristics in agreement with those reported in the literature.

1-(2,6-Diisopropylphenyl)-3-(quinolin-8-yl)-4,5-dihydro-1H-imidazol-3-ium chloride (**10**): ^1H NMR (200 MHz, $CDCl_3$) δ 9.62 (s, 1H), 8.74 (s, 1H), 8.28 (d, J = 7.9 Hz, 1H), 7.99 (d, J = 7.4 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.66 – 7.36 (m, 3H), 7.24 (d, J = 7.6 Hz, 2H), 5.24 (t, J = 10.5 Hz, 2H), 4.57 (t, J = 10.5 Hz, 2H), 3.17 (hept, J = 13.2, 6.9 Hz, 2H), 1.26 (t, J = 6.9 Hz, 12H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 158.36, 150.58, 146.73, 140.17, 137.79, 131.80, 131.72, 130.20, 129.42, 128.06, 127.01, 125.34, 122.84, 122.27, 53.35, 29.07, 25.48, 24.44. HRMS (ESI) m/z calculated for $C_{12}H_{10}O_4Na$ $[M]^+$ requires m/z 358.5085. Found m/z: 358.2321.

Cinnamyl 3-phenylpropiolate (**4a**):[22c] Prepared according to the general procedure and obtained in 97% yield (127 mg, 0.485mmol).^1H NMR (200 MHz, $CDCl_3$) δ 7.70 – 7.52 (m, 2H), 7.51 – 7.16 (m, 8H), 6.74 (d, J = 15.8 Hz, 1H), 6.34 (dt, J = 15.9, 6.5 Hz, 1H), 4.90 (d, J = 6.5 Hz, 2H).^{13}C NMR (50 MHz, $CDCl_3$) δ 154.0, 136.2, 135.5, 133.2, 130.9, 128.8, 128.8, 128.5, 126.9, 122.3, 119.7, 86.8, 80.7, 66.7.

2-Methoxy-2-oxoethyl 3-phenylpropiolate (**4b**): Prepared according to the general procedure and obtained in 25% yield (27 mg, 0.125mmol).^1H NMR (200 MHz, $CDCl_3$) δ 7.65 – 7.56 (m, 2H), 7.48 – 7.32 (m, 3H), 4.76 (s, 2H), 3.80 (s, 3H).^{13}C NMR (50 MHz, $CDCl_3$) δ 167.7, 153.4, 133.4, 131.2, 128.8, 119.3, 88.4, 79.9, 61.7, 52.8. HRMS (ESI) m/z calculated for $C_{12}H_{10}O_4Na$ $[M+Na]^+$ requires m/z 241.0579. Found m/z: 241.0472.

2-Ethoxy-2-oxoethyl 3-phenylpropiolate (**4c**):[22c] Prepared according to the general procedure and obtained in 28% yield (32 mg, 0.14 mmol).^1H NMR ($CDCl_3$) δ 7.68 – 7.55 (m, 2H), 7.51 – 7.31 (m, 3H), 4.74 (s, 2H), 4.27 (q, J = 7.1 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H).^{13}C NMR ($CDCl_3$) δ 167.1, 153.4, 133.3, 131.1, 128.8, 119.4, 88.3, 79.9, 61.9, 61.8.

Allyl 3-phenylpropiolate (**4e**):[22c] Prepared according to the general procedure and obtained in 42% yield (39 mg, 0.21 mmol). ^1H NMR ($CDCl_3$) δ 7.65 – 7.52 (m, 2H), 7.50 – 7.30 (m, 3H), 5.97 (m, 1H), 5.41 (dd, J = 17.2, 1.4 Hz, 1H), 5.32 (dd, J = 10.3, 1.2 Hz, 1H), 4.73 (d, J = 5.9 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 153.9, 133.2, 131.3, 130.9, 128.8, 119.7, 119.6, 86.7, 80.6, 66.8.

3-Methylbut-2-en-1-yl 3-phenylpropiolate (**4f**):[22c] Prepared according to the general procedure and obtained in 56% yield (60 mg, 0.28 mmol).^1H NMR ($CDCl_3$) δ 7.58 – 7.30 (m, 5H), 5.44 – 5.40 (m, 1H), 4.73 (d, J = 7.4 Hz, 2H), 1.79 (s, 3H), 1.75 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 154.3, 140.8, 133.2, 130.8, 128.7, 119.8, 117.8, 86.3, 80.8, 63.1, 26.0, 18.3.

(E)-But-2-en-1-yl 3-phenylpropiolate (**4g**):[32] Prepared according to the general procedure and obtained in 94% yield (94 mg, 0.47 mmol).^1H NMR ($CDCl_3$) δ 7.65 – 7.50 (m, 2H), 7.48 – 7.27 (m, 3H), 6.01 – 5.72 (m, 1H), 5.71 – 5.51 (m, 1H), 4.63 (d, 2H), 1.72 (d, J = 6.3 Hz, 3H).^{13}C NMR ($CDCl_3$) δ 154.0, 133.1, 133.0, 130.8, 128.7, 124.4, 119.8, 86.4, 80.8, 66.9, 18.0.

Benzyl 3-phenylpropiolate (**4h**):[22i] Prepared according to the general procedure and obtained in 61% yield (72 mg, 0.30 mmol).^1H NMR (200 MHz, $CDCl_3$) δ 7.66 – 7.55 (m, 2H), 7.50 – 7.31 (m, 8H), 5.29 (s, 2H).^{13}C NMR (50 MHz, $CDCl_3$) δ 154.1, 135.1, 133.2, 130.9, 128.9, 128.9, 128.8, 128.8, 119.7, 86.9, 80.8, 67.9.

4-Methylbenzyl 3-phenylpropiolate (**4i**):[22i] Prepared according to the general procedure and obtained in 73% yield (91 mg,0.365 mmol).^1H NMR ($CDCl_3$) δ 7.63 – 7.55 (m, 2H), 7.46 – 7.32 (m, 4H), 7.22 (d, J=7.9, 2H), 5.25 (s, 2H), 2.38 (s, 3H).^{13}C NMR ($CDCl_3$) δ 154.20, 138.80, 133.25, 132.18, 130.93, 129.61, 129.08, 128.83, 119.81, 86.82, 80.86, 67.96, 21.52.

4-Chlorobenzyl 3-phenylpropiolate (**4j**):[22i] Prepared according to the general procedure and obtained in 75% yield (101 mg, 0.375 mmol).^1H NMR ($CDCl_3$) δ 7.61 – 7.51 (m, 2H), 7.50 – 7.31 (m, 7H), 5.22 (s, 2H).^{13}C NMR ($CDCl_3$) δ 153.5, 134.4, 133.3, 132.8, 130.6, 129.8, 128.7, 128.4, 119.2, 86.8, 80.2, 66.6.

4-Methoxybenzyl 3-phenylpropiolate (**4k**):[22i] Prepared according to the general procedure and obtained in 84% yield (112 mg, 0.42 mmol).^1H NMR (200 MHz, $CDCl_3$) δ 7.77 – 7.45 (m, 2H), 7.46 – 7.28 (m, 5H), 6.98 – 6.86 (m, 2H), 5.21 (s, 2H), 3.81 (s, 3H).^{13}C NMR (50 MHz, $CDCl_3$) δ 160.16, 154.22, 133.23, 130.92, 130.84, 128.81, 127.23, 119.77, 114.26, 86.75, 80.84, 67.86, 55.54.

4-(Trifluoromethyl)benzyl 3-phenylpropiolate (**4l**):[20] Prepared according to the general procedure and obtained in 59% yield (89 mg, 0.29 mmol). ^1H NMR ($CDCl_3$) δ 7.68 – 7.62 (d, J = 8.1 Hz, 2H), 7.62 – 7.57 (m, 2H), 7.56 – 7.52 (d, J = 8.1 Hz, 2H), 7.49 – 7.43 (m, 1H), 7.41 – 7.35 (m, 2H), 5.31 (s, 2H). ^{13}C NMR ($CDCl_3$) δ 153.8, 139.1, 133.3, 131.1, 128.7, 125.8, 119.5, 87.5, 80.4, 66.8.

Cinnamyl 3-(p-tolyl)propiolate (**4o**):[22c] Prepared according to the general procedure and obtained in 83% yield (115 mg, 0.41 mmol). ^1H NMR ($CDCl_3$) δ 7.48 (d, J = 7.9 Hz, 2H), 7.41 – 7.24 (m, 5H), 7.16 (d, J = 7.9 Hz, 2H), 6.71 (d, J = 15.9 Hz, 1H), 6.32 (dt, J = 15.9, 6.6 Hz, 1H), 4.87 (d, J = 6.6 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 153.9, 141.3, 136.0, 135.2, 133.0, 129.4, 128.6, 128.2, 126.7, 122.1, 116.4, 87.2, 80.2, 66.4, 21.7.

Cinnamyl 3-(m-tolyl)propiolate (**4p**): Prepared according to the general procedure and obtained in 82% yield (113 mg, 0.41 mmol). ^1H NMR (200 MHz, $CDCl_3$) δ 7.73 – 7.08 (m, 9H), 6.74 (d, J = 15.9 Hz, 1H), 6.34 (dt, J = 15.9, 6.5 Hz, 1H), 4.90 (d, J = 6.5 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 154.1, 138.6, 136.2, 135.5, 133.7, 131.9, 130.4, 128.9, 128.7, 128.5, 126.9, 122.3, 119.5, 87.2, 80.4, 66.7, 21.4. HRMS (ESI) m/z calculated for $C_{19}H_{16}O_2Na^+$ $[M+Na]^+$ requires 299.1150. Found m/z: 299.1047.

Cinnamyl 3-(4-methoxyphenyl)propiolate (**4q**):[22c] Prepared according to the general procedure and obtained in 87% yield (123 mg, 0.43 mmol). ^1H NMR (200 MHz, $CDCl_3$) δ 7.54 (d, J = 8.9 Hz, 2H), 7.47 – 7.23 (m, 5H), 7.01 – 6.81 (m, 2H), 6.79 – 6.66 (m, 1H), 6.33 (dt, 1H), 4.88 (d, J = 6.5 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 161.8, 154.3, 136.2, 135.4, 135.2, 128.9, 128.5, 126.9, 122.4, 114.5, 111.4, 87.7, 80.2, 66.6, 55.6.

Cinnamyl 3-(4-methoxy-2-methylphenyl)propiolate (**4r**): Prepared according to the general procedure and in 91% yield (136 mg, 0.45mmol). ^1H NMR (200 MHz, $CDCl_3$) δ 7.50 (d, J = 8.4 Hz, 1H), 7.46 – 7.21 (m, 5H), 6.82 – 6.63 (m, 3H), 6.34 (dt, J = 15.9, 6.5 Hz, 1H), 4.89 (dd, J = 6.5, 1.1 Hz, 2H), 3.80 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 161.6, 154.4, 144.8, 136.2, 135.5, 135.3, 128.8, 128.4, 126.9, 122.5, 115.6, 111.9, 111.5, 86.8, 83.8, 66.6, 55.5, 21.1. HRMS (ESI) m/z calculated for $C_{20}H_{18}O_3Na^+$ $[M+Na]^+$ requires 329.1256. Found m/z: 329.1158.

Cinnamyl 3-(4-(trifluoromethyl)phenyl)propiolate (**4s**):[22c] Prepared according to the general procedure and obtained in 91% yield (150 mg, 0.45 mmol). ^{1}H NMR ($CDCl_3$) δ 7.67 (d, J = 8.2 Hz, 2H), 7.61 (d, J = 8.2 Hz, 2H), 7.41 – 7.23 (m, 5H), 6.72 (d, J = 15.9 Hz, 1H), 6.32 (dt, J = 15.9, 6.6 Hz, 1H), 4.90 (d, J = 6.6 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 153.4, 135.9, 135.7, 133.2, 132.2, 128.7, 128.4, 126.8, 125.6, 123.4, 121.9, 121.8, 84.3, 82.1, 66.9.

(E)-But-2-en-1-yl 3-(4-methoxyphenyl)propiolate (**4t**):[33] Prepared according to the general procedure and obtained in 64% yield (74 mg, 0.32 mmol). ^{1}H NMR ($CDCl_3$) δ 7.51 (d, J=9.0 Hz, 2H), 6.86 (d, J=9.0 Hz, 2H), 5.85 (dq, J=15.0, 6.5 Hz, 1H), 5.64 (dt, J=15.0, 6.5 Hz, 1H), 4.63 (d, J=6.5 Hz, 2H), 3.81 (s, 3H), 1.73 (d, J=2.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 161.4, 154.1, 134.9, 132.6, 124.2, 114.2, 111.3, 87.1, 80.0, 66.5, 55.3, 17.7.

(E)-But-2-en-1-yl 3-(p-tolyl)propiolate (**4u**):[33] Prepared according to the general procedure and obtained in 73% yield (78 mg, 0.36 mmol). ^{1}H NMR ($CDCl_3$) δ 7.46 (d, J=8.5 Hz, 2H), 7.15 (d, J=8.5 Hz, 2H), 5.85 (dq, J=15.0, 7.0 Hz, 1H), 5.64 (tq, J=15.0, 7.0 Hz, 1H), 4.63 (d, J=7.0 Hz, 2H), 2.36 (s, 3H), 1.73(d, J=7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 154.0, 141.2, 132.9, 132.7, 129.3, 124.2, 116.5, 86.8, 80.2, 66.6, 21.7, 17.6.

Computational details. The computational details of the calculations carried out are provided at the supporting information of this article.

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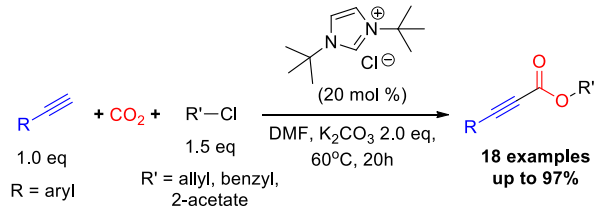

A straightforward organocatalytic method for the direct carboxylation of terminal alkynes towards propargylic esters, is reported. A simple, widely-available, stable, and cost-efficient *N*-heterocyclic carbene precursor salt was used as the (pre)catalyst.

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Unprecedented multicomponent organocatalytic synthesis of propargylic esters via CO_2 activation

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